1,3,5-triphenylpentane under the experimental conditions. The *intrinsic* rate of quenching of the DA exciplex (k_r) may be estimated from k_q for toluene (5.6×10^5 M^{-1} s^{-1}) and the relationship $k_r \cong k_q(k_{-e}/k_e)$. Since $k_e \cong k_{\text{diffusion}}$, (k_{-e}/k_e) is expected to be close to or smaller than unity so that $k_r \leq k_q$ for toluene. Accordingly, $k_{\text{con}} > k_r$, which allows multifunctional quenching to be an operative mechanism in these systems.

It is not possible to determine from the current data whether the measured k_q's for the 1,3- and 1,3,5-systems reflect k_r' or k_{con}. For example, if $k_r' > k_{\text{con}}$, conformation interchange would be the rate-limiting step for multifunctional quenching.

The data in Table I indicate that the 1,2-, 1,4-, and 1,5-diphenylalkanes show lesser degrees of enhanced quenching reactivity than the 1,3-system. With 1,2-diphenylethane, conformational interchange should be much faster than in the 1,3 system, but the inability to achieve the preferred excimer-like geometry retards the *intrinsic* quenching step. Slower rates of conformational interchange in the 1,4- and 1,5-systems,[27] as well as steric strain considerations in the excimer-like structure, may inhibit multifunctional quenching.

The Methoxy-Substituted Diphenylalkane Quenchers. In contrast to the diphenylalkanes, the methoxy-substituted difunctional aromatic quenchers show little enhanced reactivity relative to *p*-methylanisole. However, to the extent that there is enhanced quenching, the 1,3-system again is a better quencher than the 1,2-system.

This modest quenching enhancement may simply result from the more competitive nature of k_r and k_{con} in the mono- and bis-methoxy systems. Note that the monofunctional model quencher, *p*-methylanisole, displays a k_q almost two orders of magnitude greater than toluene so $k_r \cong 10^7$–10^8 s^{-1}.

An upper estimate of k_{con} for the bis-methoxy system is available from fluorescence data on *p*-methylanisole. From the fluorescence lifetime of the locally excited monomer state (9 ns[28]) and the absence of excimer formation in **3b**, it appears that $k_{\text{con}} < 10^8$ s^{-1}. Accordingly, in the methoxy-substituted systems $k_r > k_{\text{con}}$ so most of the quenching occurs by way of the DA exciplex.

Conclusions. Quenching of the benzophenone triplet state by multifunctional aromatic quenchers involves both DA and DDA exciplexes. The initially formed DA exciplex dominates the quenching when its deactivation rate is much faster than conformational interchange, as is the case with the *p*-methoxy systems. When k_{con} is much faster than deactivation of the DA exciplex, the DDA exciplex intervenes. The enhanced quenching within the triple complex results from a greater CT contribution. The structural features of the DD component seem similar to those of intramolecular excimers with the aromatic rings being in parallel planes 3–4 Å apart.

Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, and to the USC Faculty Research and Innovation Fund for their support of this work.

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(27) With the fluorescence lifetime of toluene (34 ns[28]) as a model for the lifetime of the locally excited phenyl π,π^* state in 1,4-diphenylbutane and 1,5-diphenylpentane, the absence of excimer fluorescence implies $k_{\text{con}} < 10^7$ s^{-1}.

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Ground-State Dimers in Excimer-Forming Bichromophoric Molecules. 1. Bis(pyrenylcarboxy)alkanes[‡]

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Abstract: ^{1}H NMR spectra of the 1,*n*-bis(1-pyrenylcarboxy)alkanes (1PC(*n*)1PC) and 1,*n*-bis(2-pyrenylcarboxy)alkanes (2PC(*n*)2PC) with *n* = 1–16, 22, and 32 were measured in chloroform-*d* at room temperature. From the changes in chemical shift of the aromatic protons in 2PC(*n*)2PC, as compared to the hexyl ester of 2-pyrenecarboxylic acid, it is concluded that an intramolecular ground-state dimer is present for *n* = 3–16, 22, and 32, a sandwich dimer for *n* > 8, and a shifted symmetric dimer for *n* = 3–8. With 1PC(*n*)1PC, dimer formation is found for *n* = 3–16: predominantly an asymmetric dimer, next to a symmetric one (especially for *n* = 3–7). The solvent dependence of the dimer formation (2PC(5)2PC) can be correlated with the Hildebrand solubility parameter. Variation of temperature has practically no influence (1PC(5)1PC). The conclusions based on the NMR data are confirmed by time-resolved (picosecond) excimer fluorescence measurements. In the case of 2PC(3)2PC, the presence of a ground-state dimer is seen from the dependence of its fluorescence spectrum on the excitation wavelength. In the series of 1PC(*n*)1PC and 2PC(*n*)2PC as well as with the dipyrenylalkanes 1Py(*n*)1Py and 2Py(*n*)2Py mutual through-bond interactions of the aromatic end groups are detected up to *n* = 8.

Excimers and exciplexes are generally defined as bimolecular species only existing in the electronically excited state,[1] setting them apart from dimers, EDA complexes, and other molecular aggregates in the ground state.[1b,2] This sharp distinction does not universally hold, however, as in a number of systems ground-state dimers have been detected next to the excimers.[3] Information on the absence or presence of excimer-like ground-

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[‡] Dedicated to Professor Anton Stier on the occasion of his 60th birthday.

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(1) Concerning the definitions of "excimer" or "exciplex" see: (a) *Molecular Luminescence*; Lim, E. C., Ed.; Benjamin: New York, 1969; p 907. (b) Birks, J. B. *Photophysics of Aromatic Molecules*; Wiley-Interscience: New York, 1970. (c) An excimer or exciplex can be defined as a species, made up of at least two molecules, existing in the excited state. Whether or not a dimer is present in the ground state does not directly reflect on the excimer or exciplex.

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state dimers is essential in the analysis of excimer kinetics, as different kinetic schemes and equations apply in the two cases.[3c] These differences originate from the fact that the dimers can absorb part of the excitation light, thereby forming excimers directly, circumventing the otherwise necessary diffusional processes.

The presence of ground-state dimers can reveal itself in a number of ways: (a) the sum of the preexponential factors (amplitudes) in the multiexponential response functions of the time-resolved excimer fluorescence deviates from zero;[3] (b) differences occur in the values for the rate constant of excimer formation derived either from fluorescence intensity or from decay time measurements;[4-6] (c) ring current effects on the proton chemical shifts of the aromatic end groups in molecules forming intramolecular excimers are found;[3c] and (d) new bands appear in the absorption spectra.[2,7] The first three of these experimental criteria will now be discussed, whereas the last one will be treated later in this paper.

When the excimer concentration at the moment of excitation can be neglected, this boundary condition results in a value of zero for the amplitude sum in the excimer fluorescence response function.[1b,8] Examples of bichromophoric systems for which such a behavior has been reported are 1,3-di(1-pyrenyl)propane,[9] 1Py(3)1Py, and 1,3-di(2-pyrenyl)propane,[10] 2Py(3)2Py. Excimer amplitude sums different from zero, on the other hand, have been measured with the meso diastereomer of 2,4-di(2-pyrenyl)pentane, *meso*-2DPP.[3] It was shown, employing a combination of time-correlated single-photon counting and ^{1}H NMR measurements, that with *meso*-2DPP in toluene at room temperature at least 10% of the molecules exists in the form of intramolecular ground-state dimers.[3c] For the 1,*n*-bis(1-pyrenylcarboxy)alkanes, 1PC(*n*)1PC, where *n* represents the number of CH_2 groups in the alkane chain, the excimer amplitudes likewise do not sum to zero for *n* = 3–16, 22, and 32 in methylcyclohexane.[11] Similar results were obtained with the 1,*n*-bis(2-pyrenylcarboxy)alkanes, 2PC(*n*)2PC, for *n* = 3–16 in toluene.[11] This leads to the assumption that intramolecular ground-state dimers are also present with the bis(pyrenylcarboxy)alkanes.

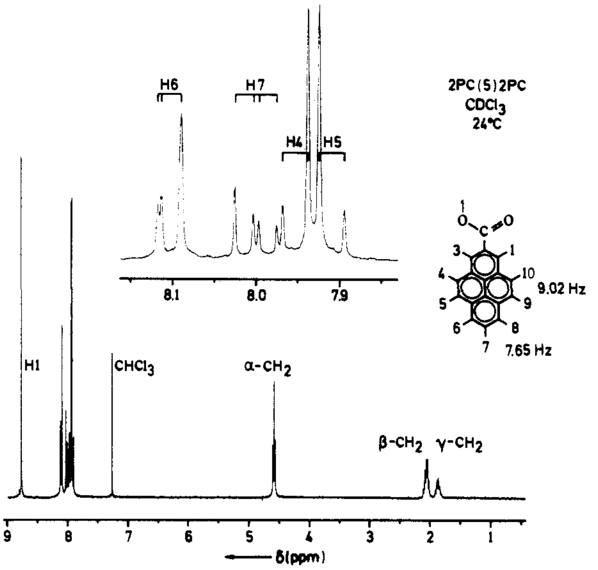

Figure 1. ^{1}H NMR spectrum of 1,5-bis(2-pyrenylcarboxy)pentane (2PC(5)2PC) in chloroform-*d* at 24 °C. A subspectrum of the aromatic protons is presented on an extended scale.

Further support for this conclusion comes from a comparison of results from photostationary and time-resolved measurements. From the unquenched-to-quenched monomer fluorescence intensity ratio I_0/I as well as from the related monomer decay time ratio τ_0/τ, the rate constant k_a of excimer formation can be determined.[4-6] When different k_a values are obtained with the two methods, this can be an indication for the presence of ground-state dimers.[5] Such differences were in fact observed for the 1PC(*n*)1PC compounds.[11]

Before the kinetics of intramolecular excimer formation with the bis(pyrenylcarboxy)alkanes can be treated, employing data derived from time-resolved fluorescence measurements, direct experimental information on ground-state interactions between the end groups of the bis(pyrenylcarboxy)alkanes is needed. This is necessary to ascertain whether the phenomena described above for the bis(pyrenylcarboxy)alkanes are indeed due to intramolecular ground-state dimers and not, for instance, to conformers in which the end groups still need a small displacement to form an excimer. Therefore, the present NMR study of the series 1PC(*n*)1PC and 2PC(*n*)2PC was undertaken. For comparative purposes, the 1,*n*-dipyrenylalkanes 1Py(*n*)1Py and 2Py(*n*)2Py were also investigated.[12] Similar to the dipyrenylpropanes, already mentioned above, excimer amplitude sums practically equal to zero have been found for both series of dipyrenylalkanes.[9,10,12]

The analysis of the ^{1}H NMR spectra of the bichromophoric compounds was carried out under the assumption that dimer formation would show up as a mutual ring current effect on the chemical shifts of the H-atoms of the pyrenyl end groups. It was expected that, in addition, information on the dimer structure would be accessible from the relative magnitude of this effect for the various aromatic protons. The influence of ring currents on proton chemical shifts has been widely studied since the phenomenon was first described by Pauling in 1936.[13] A well-known example of such a ring current effect is the strong deshielding experienced by the protons of aromatic hydrocarbons.[14] Ring

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(6) The rate constant k_a of an intramolecular reaction between a molecule in the excited state M* and a quencher Q, when ground-state dimers do not have to be taken into account (dynamic or Stern–Volmer quenching, see ref 1b), can be determined by measuring (a) the fluorescence decay time τ or (b) the fluorescence intensity I, in both cases with respect to the unquenched fluorescence lifetime τ_0 or the unquenched fluorescence intensity I_0 of M* (both from a model compound such as PC(6) in this paper, see text). When thermal dissociation of the reaction product (e.g., an excimer) can be neglected, the following equations apply: (a) $\tau_0/\tau = 1 + k_a\tau_0$ and (b) $I_0/I = 1 + k_a\tau_0$. In reactions where ground-state dimers play a role (static quenching), however, different expressions for τ_0/τ and I_0/I result, containing the equilibrium constant of dimer formation, see refs 1b, 4, and 5. When the Stern–Volmer equations are used in such a case, ignoring the existence of ground-state dimers, this then leads to differences between the k_a values derived either from fluorescence intensity or from decay time measurements.

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current effects have also been employed in investigations of micellar structure. In these studies, the influence exerted by aromatic probe molecules such as pyrene and naphthalene on the chemical shifts of the protons along the alkane chain of the surfactants was measured.[15]

Experimental Section

The synthesis of the compounds treated in this paper has been described previously[10] or will be published elsewhere.[10] 2-Phenylpyrene was a gift of Professor Ch. Jutz, Universität München.[16] 2,7-Dimethylpyrene and the [*n.n*](2,7)pyrenophanes with *n* = 2, 3, and 4 were provided by Professor H. A. Staab, Max-Planck-Institut für Medizinische Forschung, Heidelberg.[17]

The concentration of the solutions (chloroform-*d*, Merck, 99.9% D; toluene-d_8, Aldrich, 99.96% D; and octane-d_{18}, Aldrich, D > 98%) used in the ^1H NMR measurements was on the order of 2×10^{-3} M. At these concentrations, intermolecular interactions can be excluded, as deduced from NMR spectra of pyrene and 1-methylpyrene as a function of concentration.[3a,12b] Tetramethylsilane was used as internal standard. The signal of chloroform appears at 7.261 ± 0.001 ppm.

The ^1H NMR spectra (samples thermostated at 24 °C, unless otherwise indicated) were measured on a Bruker MSL 300 (300 MHz) spectrometer. Under normal conditions, the experimental accuracies are 0.002 ppm for the chemical shifts and 0.03 Hz for the coupling constants. The time-correlated single-photon counting (SPC) measurements were performed by using picosecond laser excitation. The laser system (Coherent) consisted of an Argon-Ion laser (Innova 100-10), a dye laser (702-1CD), and a frequency doubler (KDP, 298 nm; $LiJO_3$, 330 nm). The analysis of the fluorescence decays, utilizing the method of modulating functions,[18] was carried out as described previously.[3,9,10] The substances used in the SPC experiments were purified by HPLC.

Results and Discussion

Analysis of the NMR Spectra. The ^1H NMR spectra of 2PC(5)2PC and 1PC(3)1PC are depicted in Figures 1 and 2, as representatives of the two series of bis(pyrenylcarboxy)alkanes. In the spectrum of 2PC(5)2PC (Figure 1) three groups of lines occur in the range of the aliphatic protons (0–5 ppm). These protons can be identified as follows: α-CH_2 (4.582 ppm), β-CH_2 (2.059 ppm), and γ-CH_2 (1.873 ppm). In the region of the aromatic protons (around 8 ppm) a singlet is observed at 8.760 ppm, which is assigned to H1/H3, showing that the rotation between the pyrenyl and carboxy groups is not hindered on the NMR time scale. The large downfield shift of this proton by around 0.7 ppm as compared to the other aromatic protons is caused by the inductive effect of the carboxy group, see below, similar to what is found for other carboxy-substituted aromatic hydrocarbons.[19] The other signals (insert, Figure 1) correspond to an AB_2 subspectrum (H7(=A) and H6/H8(=B_2)) and an AB subspectrum (H4/H5). The chemical shifts and couplings in the AB_2 system were determined by computer simulation.[14] The, by its nature, somewhat problematic identification of the protons H4 and H5 in the AB system is based here on the assumption that the perturbation of a substituent on the proton chemical shifts decreases with increasing separation, i.e., the change in chemical shift is larger for H4 than for H5.

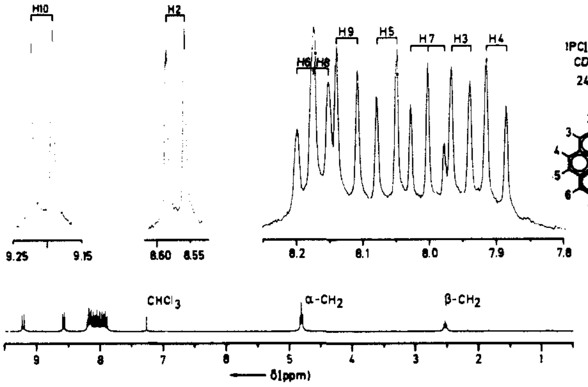

Figure 2. ^1H NMR spectrum of 1,3-bis(1-pyrenylcarboxy)propane (1PC(3)1PC) in chloroform-*d* at 24 °C. Subspectra of the aromatic protons are presented on an extended scale.

In the spectrum of 1PC(3)1PC (Figure 2), the aliphatic protons lead to a triplet at 4.806 ppm for the α-CH_2 and a quintet at 2.527 ppm for the β-CH_2 groups. In the part of the spectrum where the aromatic protons appear, between 7.5 and 9.5 ppm, two doublets are strongly shifted toward large ppm values. These must originate from the protons H2 and H10, next to the carboxy substituent, which are expected to undergo the largest changes in chemical shift, similar to H1 in 2PC(5)2PC discussed above. The coupling of 8.16 Hz for the doublet at 8.579 ppm, as compared to a coupling of 9.44 Hz for the doublet at 9.216 ppm, immediately assigns the doublets to H2 and H10, respectively. This identification is based on the well-established notion that bonds with double bond character, such as (9,10) and (4,5) in pyrenes have larger values for their vicinal coupling constants than the other more purely aromatic bonds ((2,3) and (6,7)).[20] Generally, the coupling $^3J_{9,10}$ has a value around 9 Hz, whereas $^3J_{12}$ falls around 8 Hz.[20,21] Once H10 and H2 are known, their coupling partners H9 and H3 can be found. The two remaining doublets with couplings larger than 9 Hz can then be attributed to H4 and H5 (Figure 2). A specific identification of this doublet to either H4 or H5 can again not be made with certainty. However, as in 1PC(3)1PC, different from 2PC(5)2PC, H5 is in an amphi position with respect to the carboxy group, and this proton will be affected more strongly (i.e., shifted toward larger ppm) than H4.[22,23] Besides the three AB systems (H2/H3, H4/H5, H9/H10), the remaining lines form an ABX subspectrum (H6/H8, H7), which is analyzed via computer simulation.[14] The final assignment of the protons is depicted in Figure 2.

The chemical shifts for the various protons of the pyrenylcarboxy end groups and their coupling constants are collected in Table I (2PC(5)2PC) and in Table II (1PC(3)1PC). Also listed in these tables are the data for the other compounds in the two series of bis(pyrenylcarboxy)alkanes with *n* = 1–16, 22, and 32 as well as for the model substances 2PC(6) and 1PC(6), the hexyl esters of the 2- and 1-pyrenecarboxylic acid. In order to facilitate subsequent discussion, the chemical shifts are plotted as a function of chain length in Figure 3 (2PC(*n*)2PC) and Figure 4 (1PC(*n*)1PC).

Chemical Shifts in Substituted Pyrenes. The differences between the chemical shifts for the aromatic protons in a number of substituted pyrenes and those in pyrene itself (Tables I–III), $\Delta\delta = \delta(PyX) - \delta(Py)$, are depicted in Figure 5. The carboxy- and alkylpyrenes serve as model substances for the PC(*n*)PC and Py(*n*)Py[12] series, respectively, whereas the phenylpyrenes illustrate the specific influence of aromatic ring currents. Comparable results have been reported for substituted benzenes, such as benzoic acid and biphenyl.[19,21]

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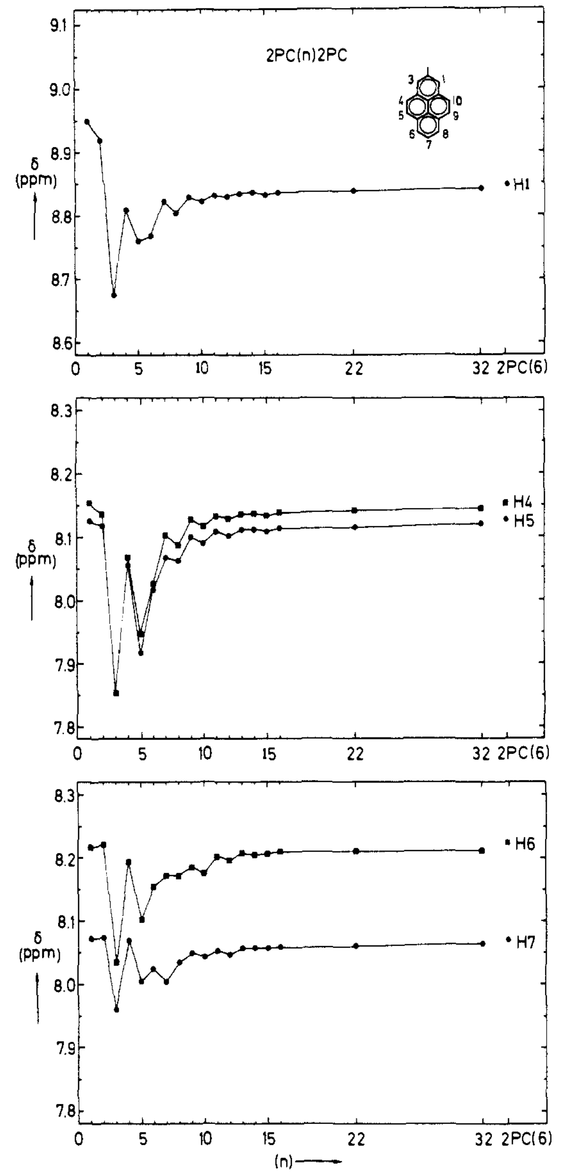

Figure 3. Chemical shifts δ (in ppm) for the aromatic protons in a series of 1,*n*-bis(2-pyrenylcarboxy)alkanes (2PC(*n*)2PC with *n* = 1–16, 22, and 32) in chloroform-*d* at 24 °C, as a function of the number of methylene groups (*n*) in the chain. The data for the model compound 2PC(6), the hexyl ester of 2-pyrenecarboxylic acid, are also given. See Table I.

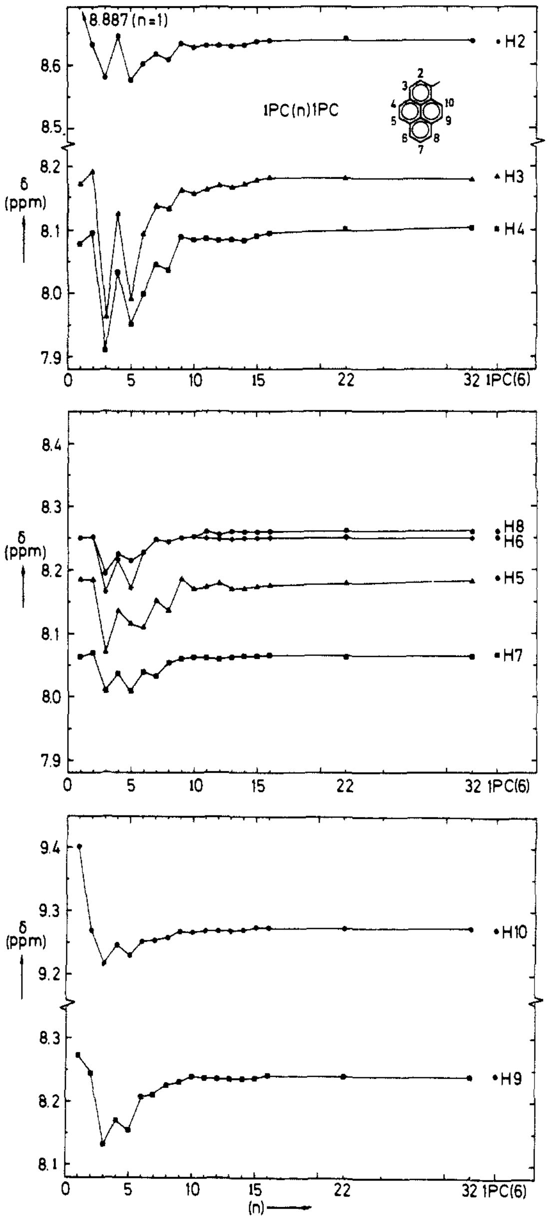

Figure 4. Chemical shifts δ (in ppm) for the aromatic protons in a series of 1,*n*-bis(1-pyrenylcarboxy)alkanes (1PC(*n*)1PC with *n* = 1–16, 22, and 32) in chloroform-*d* at 24 °C, as a function of the number of methylene groups (*n*) in the chain. The data for the model compound 1PC(6), the hexyl ester of 1-pyrenecarboxylic acid, are also given. See Table II.

The opposite sign of Δδ(H3–H7) for 2EtPy and 2PC(6), see Figure 5a, and of Δδ(H2–H8) for 1OcPy and 1PC(6), see Figure 5b, is due to the electron-repelling inductive effect (+I) of an alkyl substituent as compared to the electron-attracting inductive effect (–I) of a carboxy group.[24] In general, substituents in the 1-position of pyrene, such as with 1PC(6) and 1OcPy (Figure 5b), lead to large positive values for Δδ(H10), provided that ring current effects are not predominant (see 1-phenylpyrene, below). This is due to a steric interaction between the neighboring groups, the van der Waals (or peri) effect.[14,25] The somewhat anomalous Δδ value of H5, in comparison to H4, with 1OcPy and 1PC(6) (Figure 5b), is attributed to a mesomeric interaction, the amphi effect mentioned above.[22,23] This is also the explanation for the increase, as compared to H6, in the absolute Δδ value of H7 for 2PC(6) and 2EtPy (Figure 5a).

With 1-phenylpyrene, a chemical shift picture is obtained that is clearly different from that of 2-phenylpyrene. The differences, a shielding on the protons next to the substituent in 1-phenylpyrene (H2 and H10), are due to a ring current effect exerted by the phenyl group. The magnitude of this effect depends on the dihedral angle between the phenyl and the pyrenyl groups as well as on their relative geometries both of which are different in the two compounds (Figure 6). Molecular mechanics calculations indicate that in 1-phenylpyrene the phenyl group is oriented at an angle of 61° with respect to the pyrenyl plane, as compared to 41° in the case of 2-phenylpyrene.[26] This brings H2 and H10 of the former compound into the shielding cone of the phenyl group, which leads to a substantial reduction of the Δδ values for H2 and H10. The other protons are in the deshielding zone. In

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(23) In a 1-pyrenylcarboxy group, the amphi effect exerted by the carboxy group on the proton H5 can be visualized by drawing a quinoid resonance structure including a formal double bond between the substituent and the aromatic system. See ref 22.

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(26) The dihedral angles and rotational barriers were determined by molecular mechanics calculations (Program MMP2, Revision 6.0; Molecular Design Limited: San Leandro, Ca). For the rotational barriers between the phenyl and the pyrenyl group (0 and 90°), the following values were calculated: 1-phenylpyrene (43.2 and 2.6 kJ/mol) and 2-phenylpyrene (9.4 and 7.9 kJ/mol). With biphenyl, a dihedral angle of 40° was determined, with a rotational barrier of 8.3 kJ/mol at both 0 and 90°.

Table I. Chemical Shifts δ (in ppm) and Vicinal Coupling Constants J (in Hz) of 1,n-Bis(2-pyrenylcarboxy)alkanes (2PC(n)2PC), 2-Ethylpyrene (2EtPy), 2-Phenylpyrene (2PhPy), and the Model Compound 2-Pyrenecarboxylic Acid Hexyl Ester (2PC(6)) in Chloroform-d at 24 °C[f]

	δ (H1)	δ (H4)[a]	δ (H5)	δ (H6)	δ (H7)	$^3J_{45}$[a]	δ (α-CH$_2$)	δ (β-CH$_2$)
				2PC(n)2PC				
1	8.950	8.153	8.125	8.217	8.071	9.05	6.589	
2	8.919	8.137	8.117	8.221	8.073	9.05	4.966	
3	8.675	7.852	7.852	8.035	7.959	*b*	4.799	2.521
4	8.808	8.069	8.055	8.193	8.067	9.1	4.658	2.208
5	8.760	7.947	7.916	8.101	8.003	9.02	4.582	2.059
6	8.768	8.028	8.017	8.153	8.024	9.1	4.545	2.002
7	8.822	8.102	8.066	8.171	8.039	9.03	4.516	1.954
8	8.803	8.086	8.061	8.170	8.033	9.04	4.501	1.936
9	8.829	8.127	8.099	8.185	8.048	9.05	4.488	1.915
10	8.821	8.116	8.089	8.175	8.041	9.05	4.477	1.900
11	8.831	8.132	8.108	8.202	8.052	9.06	4.471	1.888
12	8.829	8.128	8.101	8.196	8.046	9.04	4.467	1.883
13	8.834	8.136	8.111	8.207	8.056	9.06	4.469	1.883
14	8.836	8.137	8.111	8.205	8.056	9.04	4.472	1.884
15	8.832	8.133	8.108	8.205	8.056	9.04	4.472	1.885
16	8.836	8.138	8.113	8.208	8.058	9.06	4.475	1.890
22	8.838	8.140	8.115	8.210	8.060	9.05	4.478	1.894
32	8.842	8.145	8.119	8.214	8.063	9.06	4.479	1.892
2PC(6)	8.848	8.152	8.126	8.220	8.069	9.06	4.485	1.901
2EtPy[c]	8.011	8.016	8.039	8.141	7.954	9.04	3.089	(1.464)[e]
2PhPy[d]	8.410	8.138	8.112	8.199	8.013	9.03		
				2PC(5)2PC				
(50 °C)	8.750	7.947	7.915	8.089	7.985	9.04	4.578	2.062
(5 °C)	8.768	7.953	7.921	8.109	8.014	9.01	4.586	2.070
(−35 °C)	8.781	7.959	7.928	8.124	8.033	9.02	4.592	2.075
				2PC(6)				
(50 °C)	8.831	8.131	8.103	8.196	8.043	9.06	4.485	1.899
(5 °C)	8.851	8.155	8.130	8.225	8.073	9.04	4.486	1.902
(−35 °C)	8.864	8.172	8.148	8.242	8.093	9.08	4.486	1.907

[a] The other coupling in the pyrene system, $^3J_{67}$, is equal to 7.65 Hz at 24 °C. [b] Cannot be determined due to chemical equivalence. [c] 2-Ethylpyrene. [d] 2-Phenylpyrene, NMR data for the phenyl group: δ(H) = 7.90 (o), 7.57 (m), 7.44 (p) ppm; $^3J_{o-m}$, 7.8; $^3J_{m-p}$, 7.4; $^4J_{o-p}$, 1 Hz. [e] Methyl group. [f] For 2PC(5)2PC and 2PC(6) data at three other temperatures (50, 5, and −35 °C) are given.

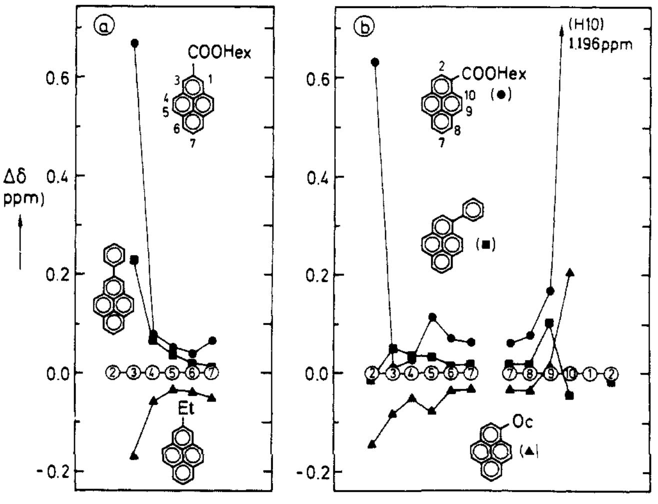

Figure 5. Differences between the chemical shifts for the aromatic protons in a number of substituted pyrenes (PyX) and those of pyrene (Py) itself: Δδ = δ(PyX) − δ(Py), Et, ethyl; Hex, hexyl; Oc, octyl. See Tables I-III.

2-phenylpyrene, all pyrenyl protons experience a deshielding ring current, due to the smaller value of the dihedral angle. This results in a Δδ pattern similar to that observed with biphenyl,[19,21] in accord with the equal values for the dihedral angles in both compounds.[26] The chemical shifts of the ortho protons in biphenyl have been shown to be mainly influenced by the ring currents of the phenyl groups, through-bond interactions apparently playing a considerably smaller role.[27] In addition, ortho–ortho proton interactions have been identified in this molecule,[27b] related to the phenomenon (peri effect) causing the increase in the Δδ value for H10 of 1PC(6) and 1OcPy, as discussed above.

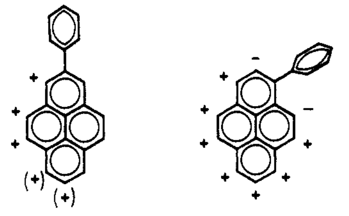

Figure 6. Schematic representations of 2-phenylpyrene (left) and 1-phenylpyrene (right), showing the deshielding (+) and shielding (−) ring current effects exerted by the phenyl substituent. See text.

[$n.n$]Pyrenophanes. The [$n.n$](2,7)pyrenophanes with $n = 3$ and 4, in which the two pyrenyl groups adopt a parallel sandwich structure, constitute realistic model system for pyrene sandwich dimers and symmetric excimers.[17b] The pyrenes in the [2.2]phane, in contrast, are strongly distorted.[17a,c,28]

The differences in the chemical shifts[17] for the aromatic protons of the pyrenophanes and those of 2,7-dimethylpyrene (Table IV) are caused by ring current effects.[14] It is seen that with $n = 4$ these differences Δδ have equal values for the two sets of protons (H3/H6) and (H4/H5), which is not the case for $n = 3$. This is in accord with the observation from X-ray analysis that the relative displacement of the pyrenes along their long axis is larger in the [3.3]phane (40 pm) than in the [4.4]analogue (17 pm).[17b] With $n = 2$, however, a large difference between Δδ(H3) and Δδ(H4) is found, which is due to the extensive distortion of the pyrenyl groups, mentioned above.

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[28] (a) Umemoto, T.; Satani, S.; Sakata, Y.; Misumi, S. *Tetrahedron Lett.* **1975**, 3159. (b) Kawashima, T.; Otsubo, T.; Sakata, Y.; Misumi, S. *Tetrahedron Lett.* **1978**, 5115.

Table II. Chemical Shifts δ (in ppm) and Vicinal Coupling Constants *J* (in Hz) of 1,*n*-Bis(1-pyrenylcarboxy)alkanes (1PC(*n*)1PC) and the Model Compound 1-Pyrenecarboxylic Acid Hexyl Ester (1PC(6)) in Chloroform-*d* at 24 °C[d]

	δ (H2)	δ (H3)	δ (H4)	δ (H5)	δ (H6)	δ (H7)	δ (H8)	δ (H9)	δ (H10)	$^3J_{23}$	$^3J_{45}$	$^3J_{67}$ = $^3J_{78}$[a]	$^3J_{9,10}$	δ (α-CH$_2$)	δ (β-CH$_2$)
1PC(*n*)1PC															
1	8.887	8.172	8.078	8.185	8.250	8.063	8.250	8.272	9.401	8.20	8.94	7.68	9.51	6.619	
2	8.632	8.191	8.096	8.184	8.252	8.068	8.252	8.243	9.268	8.17	8.97	7.68	9.45	4.997	
3	8.579	7.961	7.910	8.070	8.165	8.009	8.193	8.131	9.216	8.16	8.99	7.67	9.44	4.806	2.527
4	8.644	8.127	8.036	8.139	8.218	8.042	8.228	8.172	9.245	8.15	8.96	7.67	9.43	4.657	2.207
5	8.576	7.991	7.951	8.116	8.172	8.008	8.213	8.153	9.230	8.13	8.98	7.67	9.43	4.597	2.067
6	8.601	8.094	7.998	8.110	8.228	8.039	8.228	8.207	9.252	8.13	8.9	7.70	9.45	4.556	1.998
7	8.618	8.138	8.047	8.153	8.237	8.033	8.237	8.212	9.254	8.11	9.0	7.69	9.47	4.534	1.954
8	8.609	8.133	8.037	8.137	8.245	8.055	8.245	8.226	9.259	8.08	8.98	7.70	9.46	4.516	1.931
9	8.632	8.162	8.090	8.184	8.250	8.060	8.250	8.231	9.268	8.08	8.9	7.70	9.47	4.52	1.910
10	8.626	8.157	8.084	8.170	8.252	8.062	8.252	8.240	9.267	8.09	9.00	7.70	9.44	4.500	1.902
11	8.629	8.164	8.086	8.173	8.250	8.060	8.260	8.237	9.269	8.11	8.97	7.69	9.42	4.498	1.895
12	8.629	8.170	8.083	8.179	8.248	8.059	8.255	8.236	9.269	8.11	9.00	7.70	9.45	4.496	1.894
13	8.629	8.167	8.086	8.170	8.248	8.062	8.260	8.236	9.268	8.10	9.00	7.70	9.43	4.495	1.891
14	8.630	8.172	8.084	8.170	8.250	8.063	8.259	8.236	9.270	8.10	8.95	7.67	9.43	4.495	1.890
15	8.636	8.178	8.090	8.173	8.250	8.063	8.259	8.236	9.274	8.10	8.97	7.67	9.44	4.499	1.892
16	8.637	8.182	8.095	8.175	8.250	8.065	8.260	8.242	9.274	8.07	8.98	7.67	9.40	4.499	1.893
22	8.640	8.180	8.102	8.178	8.250	8.062	8.260	8.241	9.273	8.10	8.97	7.65	9.45	4.501	1.899
32	8.637	8.179	8.104	8.182	8.250	8.063	8.260	8.240	9.274	8.10	8.98	7.65	9.40	4.503	1.891
1PC(6)	8.635	8.185	8.101	8.187	8.250	8.066	8.260	8.242	9.271	8.11	9.00	7.67	9.45	4.51	1.907
1PC(5)1PC															
octane-d_{18}	8.544	7.756	7.719	7.899	8.028	7.843	8.028	7.984	9.413	8.02	8.99	7.66	9.47	4.524	*b*
toluene-d_8	8.660	7.677	7.592	7.741	7.804	7.676	7.846	7.901	9.684	8.15	8.95	7.68	9.49	4.351	1.650
1PC(6)															
octane-d_{18}	8.655	8.037	7.965	8.044	8.138	7.924	8.138	8.111	9.514	8.00	8.93	7.60	9.50	4.431	1.873
toluene-d_8	8.704	7.807	7.698	7.788	7.874	7.712	7.874	7.953	9.683	8.13	8.99	7.66	9.48	4.351	1.652
$CH_3COO–CH_2–OOCCH_3$														5.735	(2.122)[c]
$CH_3COO–(CH_2)_2–OOCCH_3$														4.274	(2.092)[c]
$CH_3COO–(CH_2)_5–CH_3$														4.054	(1.618)[c]

[a] $^4J_{68}$ = 1.0 ± 0.1 Hz (only observable for *n* = 2, 3, 7, 8, 16, and 22). [b] Cannot be detected next to resonance of incompletely deuterated solvent due to the very low solubility. [c] Methyl group. [d] Data for 1PC(5)1PC and 1PC(6) in octane-d_{18} and in toluene-d_8, for two diacetoxyalkanes and acetic acid hexyl ester in chloroform-*d* are also given.

Table III. Chemical Shifts δ (in ppm) and Vicinal Coupling Constants *J* (in Hz) of Pyrene and 1-Substituted Pyrenes in Chloroform-*d* at 24 °C[e,f]

	δ (H2)	δ (H3)	δ (H4)	δ (H5)	δ (H6)	δ (H7)	δ (H8)	δ (H9)	δ (H10)	$^3J_{23}$	$^3J_{45}$	$^3J_{67}$ = $^3J_{78}$[a]	$^3J_{9,10}$	δ (α-CH$_2$)	δ (β-CH$_2$)	δ (γ-CH$_2$)	δ (CH$_3$)
pyrene	8.005	8.182	8.075	8.075	8.182	8.005	8.182	8.075	8.075	7.62	8.97[b]	7.62	8.97[b]				
1MePy	7.876	8.092	8.033	8.009	8.176	7.992	8.161	8.121	8.254	7.72	9.03	7.65	9.23				2.992
1EtPy	7.896	8.126	8.034	8.011	8.163	7.985	8.156	8.110	8.301	7.82	9.02	7.63	9.28	3.378			1.553
1PrPy	7.873	8.111	8.034	8.012	8.161	7.984	8.152	8.099	8.290	7.81	8.99	7.66	9.28	3.326	1.897		1.081
1BuPy	7.872	8.108	8.031	8.009	8.161	7.983	8.151	8.100	8.290	7.80	8.99	7.66	9.29	3.346	1.845	1.51	1.000
1HxPy	7.863	8.100	8.022	8.000	8.152	7.975	8.142	8.092	8.278	7.80	8.99	7.64	9.29	3.339	1.855	1.50	0.900
1OcPy	7.860	8.098	8.023	8.000	8.150	7.973	8.140	8.090	8.276	7.79	9.01	7.65	9.30	3.336	1.853	1.49	0.879
1HxdPy	7.861	8.099	8.023	8.001	8.151	7.974	8.142	8.090	8.276	7.80	9.01	7.65	9.28	3.335	1.852	1.49	0.875
1PhPy[d]	7.992	8.234	8.107	8.107	8.193	8.021	8.196	8.175	8.030	7.99	*c*	7.61	9.51				
n-dodecane														1.28	1.26	1.26	0.881

[a] $^4J_{68}$ = 1.0 ± 0.1 Hz for all pyrene derivatives. [b] Via $^{13}C–H$ satellite spectrum (1,3,6,8-tetradeuteropyrene in carbon disulfide), see ref 25. Cannot be determined directly due to chemical equivalence. [c] Cannot be determined directly due to chemical equivalence. [d] Chemical shifts and couplings of phenyl group: 7.64 (o), 7.57 (m), 7.50 (p) ppm; $^3J_{o-m}$, 7.8; $^3J_{m-p}$, 7.4; $^4J_{o-m}$, 1 Hz. [e] Chemical shifts of *n*-dodecane are also indicated. [f] 1MePy, 1-methylpyrene; 1EtPy, 1-ethylpyrene; 1PrPy, 1-propylpyrene; 1BuPy: 1-butylpyrene; 1HxPy, 1-hexylpyrene; 1OcPy, 1-octylpyrene; 1HxdPy, 1-hexadecylpyrene; 1PhPy, 1-phenylpyrene.

For a symmetric sandwich dimer of pyrene, having a structure similar to that found for *n* = 4, a uniform Δδ pattern is likewise to be expected. Therefore, a comparison of the Δδ values of the dipyrenyl compounds studied in this paper with those of the [4.4]phane can serve to estimate the amount of dimer in bichromophoric systems where such symmetric dimers are present, see below. It is of interest to note that the –Δδ values of the pyrenophanes are considerably smaller than those found for the partial-overlap conformer in the racemic diastereomer of 2,4-di(1-pyrenyl)pentane (*rac*-1DPP)[12,29] and for the asymmetric 1,8-di(1-pyrenyl)naphthalene.[30] This may be caused by the anisotropic spatial characteristics of the shielding/deshielding cones of the aromatic moieties.[14]

Table IV. Chemical Shifts δ and Differences Δδ (in ppm), as compared to 2,7-Dimethylpyrene, of [*n.n*](2,7)Pyrenophanes with *n* = 2, 3, and 4 in Chloroform-*d* at 24 °C

	δ (H3)	δ (H4)	Δδ (H3)[a]	Δδ (H4)[a]	δ (α-CH$_2$)	δ (β-CH$_2$)
2,7-dimethylpyrene	7.970	7.976			(2.789)[b]	
[2.2](2,7)pyrenophane	7.196	7.449	–0.774	–0.527	3.492	
[3.3](2,7)pyrenophane	7.386	7.413	–0.584	–0.563	3.22	2.55
[4.4](2,7)pyrenophane	7.320	7.327	–0.650	–0.649	2.782	2.179

[a] Δδ = δ([*n.n*](2,7)pyrenophane) – δ(2,7-dimethylpyrene). [b] Methyl group.

1,*n*-Bis(2-pyrenylcarboxy)alkanes, 2PC(*n*)2PC. The chemical shifts of the aromatic protons in the series 2PC(*n*)2PC with *n* = 1–16, 22, and 32, clearly depend on chain length (Figure 3 and

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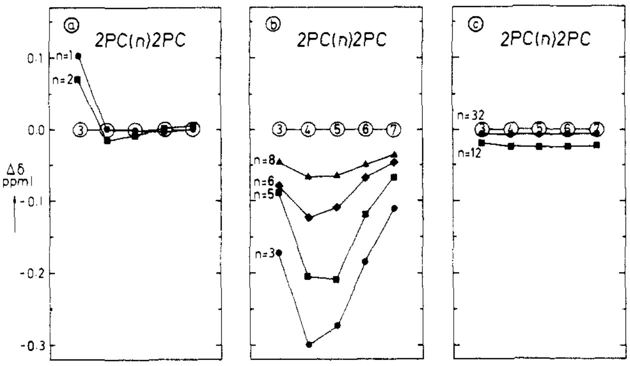

Figure 7. Differences in chemical shift Δδ (in ppm), with respect to the model substance 2PC(6), the hexyl ester of 2-pyrenecarboxylic acid, for three groups of 1,*n*-bis(2-pyrenylcarboxy)alkanes (2PC(*n*)2PC), in chloroform-*d* at 24 °C. The aromatic protons H3–H7 are indicated as circles, in a side-on view of the pyrene periphery. See Table I.

Table I). They are, with the exception of those for the proton H1(=H3) in the case of $n = 1$ and 2, shifted toward lower ppm values, as compared to the model compound 2PC(6). The largest chemical shift differences, Δδ = δ(2PC(n)2PC) - δ(2PC(6)), are found with $n = 3$ and 5 for H4 and H5 (Δδ = -0.30 ppm for H4 of $n = 3$). The shielding diminishes with increasing chain length, showing an alternating pattern with a break between $n = 5$ and 7. Even for the compound with the longest chain, 2PC(32)2PC, the effect has not yet completely disappeared.

The chemical shift patterns of the pyrenylcarboxy protons can be divided into three parts, as a function of chain length: (i) $n = 1$ and 2, (ii) $n = 3$–8, and (iii) $n = 9$–16, 22, and 32; see Figure 7, where examples for each group are depicted, showing the Δδ values for the protons along the pyrene periphery. For the longest chains (cf. Figure 3), the differences Δδ are approximately equal for all aromatic protons. This uniform pattern is not present for the compounds with intermediate chain length, for which the Δδ values of H4 and H5 become more and more predominant when going from $n = 8$ to $n = 3$. With $n = 1$ and 2, finally, only the proton H1 is affected to an appreciable extent, see Figure 7a and Table I. Such a deshielding of H1 is not found for the related compound 1PC(2)1PC, as will be discussed below. The shieldings observed for all aromatic protons of the 2PC(*n*)2PC compounds with $n > 2$, arise from a ring current effect in a conformer having the pyrenylcarboxy groups in an intramolecular dimer configuration.

Dimer Structure 2PC(*n*)2PC. The differences between the three groups of 2PC(*n*)2PC molecules described in the previous section are attributed to changes in the relative configuration of the pyrenes in the dimers. For $n = 9$–16, 22, and 32, the dimer has a symmetric sandwich structure, as all aromatic protons show shieldings of uniform magnitude, similar to what was observed for the [4.4]pyrenophane (Table IV). With the intermediate chain lengths, $n = 3$–8, the predominance of the shielding effect on H4 and H5 (Figures 3 and 7b) can be explained by a displacement of the two pyrenylcarboxy moieties along their long axis, resulting in a shifted but still symmetric dimer, similar to the structure observed with the [3.3]pyrenophane. Such a shift moves the proton H7 as well as H1 and H6 toward the deshielding zones of the two pyrenes, leading to weaker ring current effects. The deviation from symmetry for $n = 3$–8 is not surprising, as the presence of these short alkane chains restricts the possible relative configurations of the two pyrenylcarboxy groups. As the Δδ values for H4–H8 of $n = 1$ and 2 are practially zero (Figure 7a), it is concluded that a ground-state dimer is not present in these compounds. A possible contribution of through-bond interactions to the deshielding found for H1 in 2PC(1)2PC and 2PC(2)2PC will be discussed together with the data for the 1PC(*n*)1PC molecules, see below.

Dimer Concentration 2PC(*n*)2PC. The relative concentration of the ground-state dimers in the series 2PC(*n*)2PC can be estimated, as treated above, comparing the Δδ values for the proton H4 or H5 of these substances with those of [4.4](2,7)pyrenophane (Tables I and IV). A reliable indication of the extent of dimerization can only be expected for those molecules in which the configuration of the pyrenes is similar to that in the pyrenophane. This is the case for the 2PC(*n*)2PC compounds with $n > 8$, for which a symmetric dimer structure was deduced in the previous section. It must then further be assumed that the intermolecular spacings in the dimers are similar to those in the pyrenophane. The ratio of the Δδ value for the proton H4 of these 2PC(*n*)2PC molecules and those of the [4.4]pyrenophane varies between 0.06 ($n = 10$) and 0.01 ($n = 32$). This means that for $n = 10$, as an example, around 6% of the molecules are present as dimers and that even for the long-chained compounds dimer formation still takes place, down to a concentration of about 1% for $n = 32$. For the 2PC(*n*)2PC molecules with the shorter chains ($n = 3$–8), where the shieldings are considerably stronger that for the longer chains, the Δδ ratio cannot be used to estimate the dimer fraction. This is because of the fact that in the shifted dimers present in these compounds the protons H4 and H5 experience ring currents for which the [4.4]pyrenophane is not a correct model substance.

Temperature Dependence of Δδ for 2PC(5)2PC. The NMR spectra of 2PC(5)2PC and 2PC(6) were measured between 50 and -35 °C in chloroform-*d* to investigate the temperature dependence of the Δδ values and, hence, of the dimer formation. The shielding of the aromatic protons becomes larger upon lowering the temperature (Table I). As an example, -Δδ(H5) increases from 0.19 ppm at 50 °C to 0.22 ppm at -35 °C. The Δδ pattern along the pyrene periphery, however, remains the same, indicating that there is no change in dimer structure. In comparison, the -Δδ values for the protons H4 and H5 of the [4.4](2,7)pyrenophane increase with temperature in the same manner, from 0.63 to 0.65 ppm going from 50 to 10 °C.[31] For the [3.3](2,7)pyrenophane a similar behavior was observed (0.55–0.57 ppm).[31] This shows that dimer formation with 2PC(5)2PC is practically temperature independent, pointing to a ΔG value close to zero.

Absorption Spectrum of Ground-State Dimer. Support for the conclusion that ground-state dimers are present with the 1,*n*-bis(2-pyrenylcarboxy)alkanes comes from fluorescence spectra. When ground-state dimers acting as excimer precursors are absent, the excimer-to-monomer fluorescence intensity ratio I'/I does not depend on excitation wavelength. This, for example, has been observed in the case of 1Py(13)1Py.[12,31] For 2PC(3)2PC in toluene (5×10^{-6} M) at 25 °C, however, the ratio I'/I strongly changes with the wavelength of the excitation light (Figure 8). The peaks around 360, 330, and 286 nm in this excitation spectrum are therefore attributed to the dimer of 2PC(3)2PC. It should be noted that the absorption spectrum of 2PC(3)2PC is practically identical with that of 2PC(6), except for a relatively weak increase in the absorbance between 345 and 370 nm (in accord with the excitation spectrum) and a small (0.5 nm) red-shift of the vibrational peaks.

1,*n*-Bis(1-pyrenylcarboxy)alkanes, 1PC(*n*)1PC. In the series 1PC(*n*)1PC with $n = 1$–16, 22, and 32 the chemical shifts of the pyrenylcarboxy protons depend on chain length (Figure 4 and Table II), similar to what was observed for the 2PC(*n*)2PC compounds (Figure 3). The largest shieldings are found for the protons H3 and H4 of $n = 3$ and 5, Δδ = δ(1PC(*n*)1PC) - δ(1PC(6)) reaching -0.22 ppm for H3 of 1PC(3)1PC, see Figure 9b. The -Δδ values generally are somewhat smaller than those obtained for the 2PC(*n*)2PC molecules, cf. Figure 3 and Table I, a dilution effect due to the presence of different rotamers in the former molecules.[12,29]

The Δδ values for $n = 3$–8 (Figure 9b and see Figure 10, below) show an asymmetric pattern with considerably larger shieldings for the protons opposite to the substitution position of the carboxy group, especially for H3 and H4, than for H7–H10. With $n = 9$–16, 22, and 32, finally, all -Δδ values are clearly smaller than for $n = 3$–8, with somewhat larger shieldings of the protons H3–H5 than of H6–H10 (Figure 9c), and approach a value of zero for the compounds with the longest chains: $n = 22$ and 32.

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[31] Zachariasse, K. A. Unpublished results.

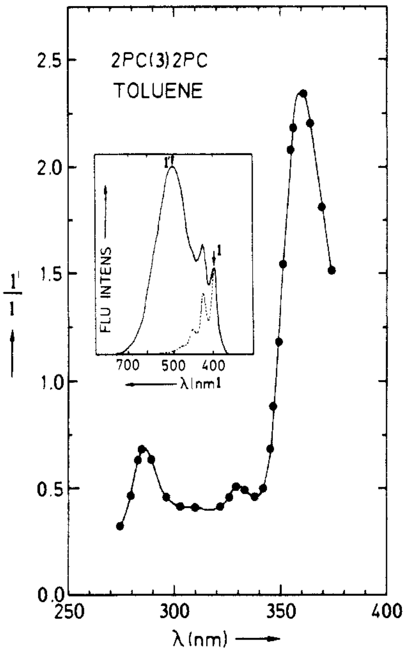

Figure 8. Plot of the excimer-to-monomer fluorescence intensity ratio I'/I of 1,3-bis(2-pyrenylcarboxy)propane (2PC(3)2PC) in toluene at 25 °C, as a function of the excitation wavelength. In the insert, the fluorescence spectrum of 2PC(3)2PC is depicted (excitation wavelength 365 nm), indicating the spectral positions where I' and I were determined.

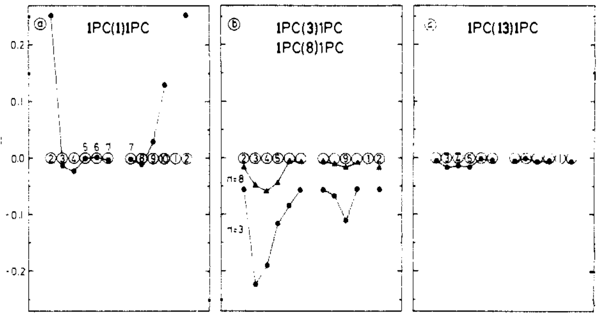

Figure 9. Differences in chemical shift Δδ (in ppm), with respect to the model substance 1PC(6), the hexyl ester of 1-pyrenecarboxylic acid, for three groups of 1,n-bis(1-pyrenylcarboxy)alkanes (1PC(n)1PC), in chloroform-d at 24 °C. The aromatic protons H2–H7 are indicated as circles, in two opposite side-on views of the pyrene periphery. See Table II.

It can therefore be stated that for all chain lengths n = 3–16, the Δδ pattern is asymmetric with respect to the long axis of the pyrene moiety. Such an asymmetry was not encountered in the series 2PC(n)2PC, for which it was concluded above that one symmetric ground-state dimer is present, changing its configuration as a function of chain length.

Dimer Structure 1PC(n)1PC. A symmetric dimer, such as found in the 2PC(n)2PC series and with the pyrenophanes, would not lead to a topological asymmetry in the Δδ values as observed with the 1PC(n)1PC compounds. Therefore, an asymmetric dimer structure is invoked, in which the long axis of one pyrenylcarboxy group is oriented at an angle with respect to that of the other, facing H9 and with maximum overlap at H3 and H4.[32] The ring currents in this dimer then lead to the relatively large negative Δδ values of H3 and H4, i.e., the asymmetric Δδ pattern (Figure 9b).

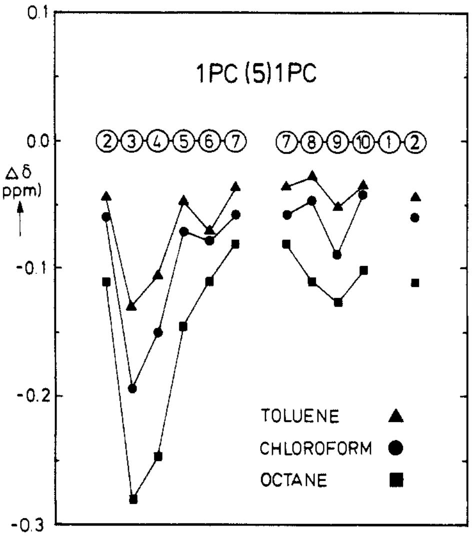

Figure 10. Differences in chemical shift Δδ (in ppm), with respect to the model substance 1PC(6), the hexyl ester of 1-pyrenecarboxylic acid, for 1,5-bis(1-pyrenylcarboxy)alkanes (1PC(5)1PC), in three solvents at 24 °C: toluene-d_8, chloroform-d, and octane-d_{18}. The aromatic protons H2–H7 are indicated as circles, in two opposite side-on views of the pyrene periphery. See Table II.

With an asymmetric dimer alone, however, in which H7 does not overlap with the other pyrenylcarboxy group, the shielding of considerable magnitude observed for H7 in the case of n = 3–7 (Figures 9b and 10 and Table II) cannot be understood. This points to the presence of a second dimer, with the pyrenylcarboxy groups in a symmetric sandwich configuration, in which all aromatic protons are equally shielded, as treated above.

That two dimers are, in principle, possible for the 1PC(n)1PC molecules finds support in the observation of two structurally different excimers in these compounds with n = 2–16,[11,33] similar to what was found with 1Py(3)1Py.[9] In the 2PC(n)2PC series for $n > 2$, in contrast, only one excimer was detected,[11] in accord with the observation of one ground-state dimer, as discussed previously. The time-resolved measurements of the bis(pyrenylcarboxy)alkanes will be further discussed in a subsequent section.

PC(1)PC and PC(2)PC. Through-Bond Interactions on Pyrenyl Protons. With 1PC(2)1PC, in contrast to its structural isomer 2PC(2)2PC (see above), Δδ is practically zero for all aromatic protons (Table II). This means that only those conformers are present in which the pyrenylcarboxy groups are too far apart to exert a ring current effect on each other, i.e., ground-state dimers are not formed. Further, it is concluded from this finding that mutual through-bond effects of the two pyrenylcarboxy groups on the chemical shifts of the pyrenyl protons can be neglected when they are separated by two methylene groups. This absence of through-bond interactions on the aromatic protons will a fortiori hold for the 1PC(n)1PC molecules with longer chains. A similar conclusion is drawn for the 2PC(n)2PC series, in which the carboxy groups are less strongly coupled to the pyrenyl group due to the nodal plane passing through the carbon atoms C2 and C7 in the frontier orbitals of pyrene.[34-36] In 2PC(2)2PC, see Figure

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[32] The proton H9 of the compounds 1PC(n)1PC with n = 3–8 experiences a considerably larger shielding than the neighboring protons H8 and H10, see Figures 9b and 10 and Table II. This cannot be explained by a ring current effect exerted by a pyrenylcarboxy group, as its size would lead to a similar influence on all three protons. The additional shielding could be due to the magnetic anisotropy (ref 14) of the much smaller carbonyl part of the carboxy group.

[33] Time-correlated single-photon counting measurements for the 1,n-bis(1-pyrenylcarboxy)alkanes 1PC(n)1PC, with n = 2–16, 22, and 32 in methylcyclohexane (MCH) and n-hexadecane at 20 °C, result in excimer fluorescence response functions that cannot be fitted with two exponentials. Fits with three exponentials lead to good results, as judged by the value of χ^2 and the auto-correlation functions, see Figures 11c and 11d. The corresponding monomer fluorescence decays are single-exponential. It is, therefore, concluded that in these 1PC(n)1PC compounds two structurally different excimers are present (ref 11).

[34] In the highest bonding and lowest antibonding orbitals of pyrene, in the Hückel approximation, a node passes through the carbon atoms C2 and C7, see ref 35.

[35] (a) Streitwieser, Jr., A. *Molecular Orbital Theory for Organic Chemists*; Wiley: New York, 1961. (b) Salem, L. *The Molecular Orbital Theory of Conjugated Systems*; Benjamin: New York, 1966.

7a, the deshielding of H1 (and the weak shielding of H4) can originate from a ring current effect in a conformer in which the two pyrenylcarboxy groups partially overlap. The strong deshielding of H1 in 2PC(1)2PC (Figure 7a) and of H2 in 1PC(1)1PC (Figure 9a) may be caused by through-bond interactions, with a contribution from ring current effects. Note that for 2PC(6) and 1PC(6) the protons H1 and H2, respectively, are also strongly deshielded (Figure 5). This was likewise explained by a through-bond interaction.

Solvent Dependence of Dimer Formation with 1PC(5)1PC. To determine the solvent dependence of the dimer formation in the bis(pyrenylcarboxy)alkanes, the $\Delta\delta$ values with respect to 1PC(6) observed for 1PC(5)1PC in chloroform-*d* are compared with those in octane-d_{18} and in toluene-d_8 (Table II). In all three solvents, a similar $\Delta\delta$ pattern for the pyrenyl protons is found (Figure 10), showing that the dimer structure is the same in the three solvents. However, the $-\Delta\delta$ values in octane-d_{18} are about 1.5 times larger than in chloroform-*d*, whereas smaller values are observed in toluene-d_8. For example, $\Delta\delta$(H3) equals −0.28 ppm in octane-d_{18} as compared to −0.19 ppm in chloroform-*d* and −0.13 ppm in toluene-d_8, meaning that the shielding and consequently the dimer formation is more pronounced in octane than in the two other solvents. This is caused by a better solvation of the pyrenylcarboxy groups in toluene and in chloroform than in octane, which counteracts dimerization. An explanation for this behavior can be obtained by considering the Hildebrand solubility parameters δ(sol).[37] The δ(sol) value of octane deviates more strongly from that of an aromatic hydrocarbon such as pyrene than do the values of the other two solvents.[9b,29,38]

Meaning of Excimer Amplitude Ratio $R = -A(-)/A(+)$. Before time-resolved fluorescence measurements will be discussed, it should be recalled[3c] that the ratio of the negative and the positive amplitudes in excimer fluorescence decays, $R = -A(-)/A(+)$, contains information on the question whether excimer-like dimers already exist in the ground state or not. This follows from an inspection of the expression for the multiexponential excimer fluorescence intensity $i_D(t)$

$$i_D(t) = k_f'[^1D^*(t)] = \textstyle\sum_i A_{2i} e^{-t/\tau_i} \tag{1}$$

where k_f' is the radiative rate constant and $[^1D^*(t)]$ is the excimer concentration at a given time.[9a] Clearly, when at $t = 0$ the excimer concentration is equal to zero, i.e., when excimer formation does not proceed via an excimer-like ground-state dimer, the sum $\sum_i A_{2i} = 0$, or, $R = -A(-)/A(+) = 1.0$.

A number of reasons exist, however, for a deviation of R from unity.[3c] These reasons are the following: (a) A preformed excimer absorbs the excitation light. Its mere presence does not have an influence on R. Therefore, R can depend on the excitation wavelength via the absorption spectrum of the dimer. (b) The monomer emission at the observation wavelength cannot be neglected. (c) An insufficient number of exponentials are used to fit the excimer fluorescence response functions. (d) The time resolution in an SPC experiment is inadequate. This is the case when the number of channels containing a decay time τ_i is too small.[9c] The time resolution primarily depends on the time per channel. In addition, it is a function of the effective width of the excitation pulse. It has been observed,[39] however, that excitation with a picosecond laser does not improve the time resolution over that obtained with a nanosecond flashlamp, when the shortest decay time is represented in one or two channels. The ratio R can only be used as a test for the presence of ground-state dimers, when (b)–(d) can be excluded.

Time-Resolved Fluorescence Measurements. As mentioned in the Introduction, evidence for the presence of ground-state dimers has been found by an analysis of the time-resolved excimer fluorescence of several bichromophoric systems. Similarly, as a support for the conclusions drawn here from the NMR experiments, a number of representative excimer fluorescence response functions of the bis(pyrenylcarboxy)alkanes will be presented. The complete set of the SPC data (monomer and excimer) for the series 1PC(*n*)1PC and 2PC(*n*)2PC will be discussed separately.

For 2PC(6)2PC in toluene (Figure 11a), the ratio $R = -A(-)/A(+)$ in the double-exponential excimer fluorescence at 520 nm strongly deviates from unity ($R = 0.82$). Similar results are obtained for the other 2PC(*n*)2PC molecules with n = 3–16,[31] see 2PC(13)2PC in Figure 11b ($R = 0.80$, in toluene). In the triple-exponential excimer fluorescence decays[33] of the compounds 1PC(*n*)1PC with n = 3–16, 22, and 32, the amplitude ratio R likewise is smaller than 1.0.[11] Examples are given in Figure 11 (parts c and d), where the excimer rise and decay curves of 1PC(5)1PC in *n*-octane ($R = 0.69$) and 1PC(12)1PC in methylcyclohexane ($R = 0.86$) are depicted.[35] These SPC results fully confirm the conclusions presented in the previous sections, based on ring current effects in the NMR spectra, that ground-state dimers are present for the 2PC(*n*)2PC and the 1PC(*n*)1PC molecules with n = 3–16.

With 1PC(2)1PC in various solvents, however, the ratio R has a value close to unity.[11] This is what should be expected when ground-state dimers are not involved in the excimer formation, as deduced from the absence of ring current effects in this compound (see above). For 2PC(1)2PC, 2PC(2)2PC, and 1PC(1)1PC, finally, excimer fluorescence is not observed at room temperature,[31] supporting the conclusion that the nonzero $\Delta\delta$ values in these molecules (Figures 7a and 9a) are not due to dimer formation.

Through-Bond Interaction on Vicinal Coupling Constants. The vicinal coupling constant $^3J_{23}$ of the molecules 1PC(*n*)1PC with n = 1–3 is larger[40] than the mean value of 8.10 Hz found for the compounds with longer chains (n = 7–32) and for 1PC(6) (Table II). For $^3J_{9,10}$, only with $n = 1$, a deviation from the mean value of 9.44 Hz obtained with the other chain lengths is observed. The remaining coupling constants, $^3J_{45}$ and $^3J_{67}$, do not depend on n. Similarly, in the series 2PC(*n*)2PC, the couplings $^3J_{45}$ and $^3J_{67}$ are independent of chain length (Table I). These results show that for $n = 1$ and to a smaller extent also for n = 2 and 3, the pyrenylcarboxy groups in the 1PC(*n*)1PC molecules exert a through bond interaction on each other, affecting the pyrenyl bonds (2,3) and (9,10) closest to the substitution position. This then leads to larger couplings for these bonds and hence to an increase in their double bond character.[20]

Methylene Chains. Through-Bond Interactions. The chemical shifts of the α- and β-CH$_2$ groups in the alkane chains of the bis(pyrenylcarboxy)alkanes 1PC(*n*)1PC and 2PC(*n*)2PC and of the model substances 1PC(6) and 2PC(6) are depicted as a function of chain length in Figure 12 (cf. Tables I and II).[41] It is seen that $\delta(\alpha\text{-CH}_2)$ for the shorter chains (n = 1–8) is shifted to larger ppm values as compared to the mean value 4.48 ppm obtained for the longer chains, the shift decreasing with the increasing number of methylene groups. For the β-CH$_2$, this downfield shift is found up to $n = 9$. Note that practically identical shift patterns for the α- and β-CH$_2$ groups are observed with both PC(*n*)PC series.

These downfield shifts can in principle originate from two effects, both coming from the second pyrenylcarboxy group in the PC(*n*)PC molecules. First, an electronic perturbation acting

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(36) The difference in the influence of substituents in either the 1- or the 2-position on the molecular properties of pyrenes can also be seen from the observation that the fluorescence lifetime τ_0 of 1-ethylpyrene (245 ns, in methylcyclohexane at 25 °C, ref 31) shows a larger decrease compared to pyrene (446 ns, ref 31) than does 2-ethylpyrene (367 ns, ref 10).

(37) (a) Hildebrand, J. H. *The Solubility of Non-Electrolytes*, 3rd ed.; Reinhold: New York, 1975. (b) Burrell, H. In *Polymer Handbook*; Brandup, J., Immergut, E. H., Eds.; Wiley: New York, 1975; Vol. IV, p 337. (c) Barton, A. F. M. *CRC Handbook of Solubility Parameters and Other Cohesion Parameters*; CRC Press: Boca Raton, FL, 1983.

(38) The Hildebrand solubility parameters δ(sol) employed in the text have the following values, in (cal/cm^3)$^{1/2}$: 7.6 (octane); 8.9 (toluene); 9.3 (chloroform); 9.2–9.9 (aromatic hydrocarbons). See ref 37.

(39) Leinhos, U.; Piehl, Th.; Zachariasse, K. A. Unpublished results.

(40) The couplings $^3J_{23}$ of the 1PC(*n*)1PC molecules with n = 1–3 are at least 0.06 Hz larger than the mean value of 8.10 Hz for the compounds with n = 7–32. The experimental accuracy is 0.03 Hz, see Experimental Section.

(41) Included in Figure 12 are data on the methylene chemical shifts for the dipyrenylalkanes 1Py(*n*)1Py (n = 1–10 and 13) and 2Py(*n*)2Py (n = 1–10 and 14), taken from ref 12, and for a number of 1-alkylpyrenes (Table III).

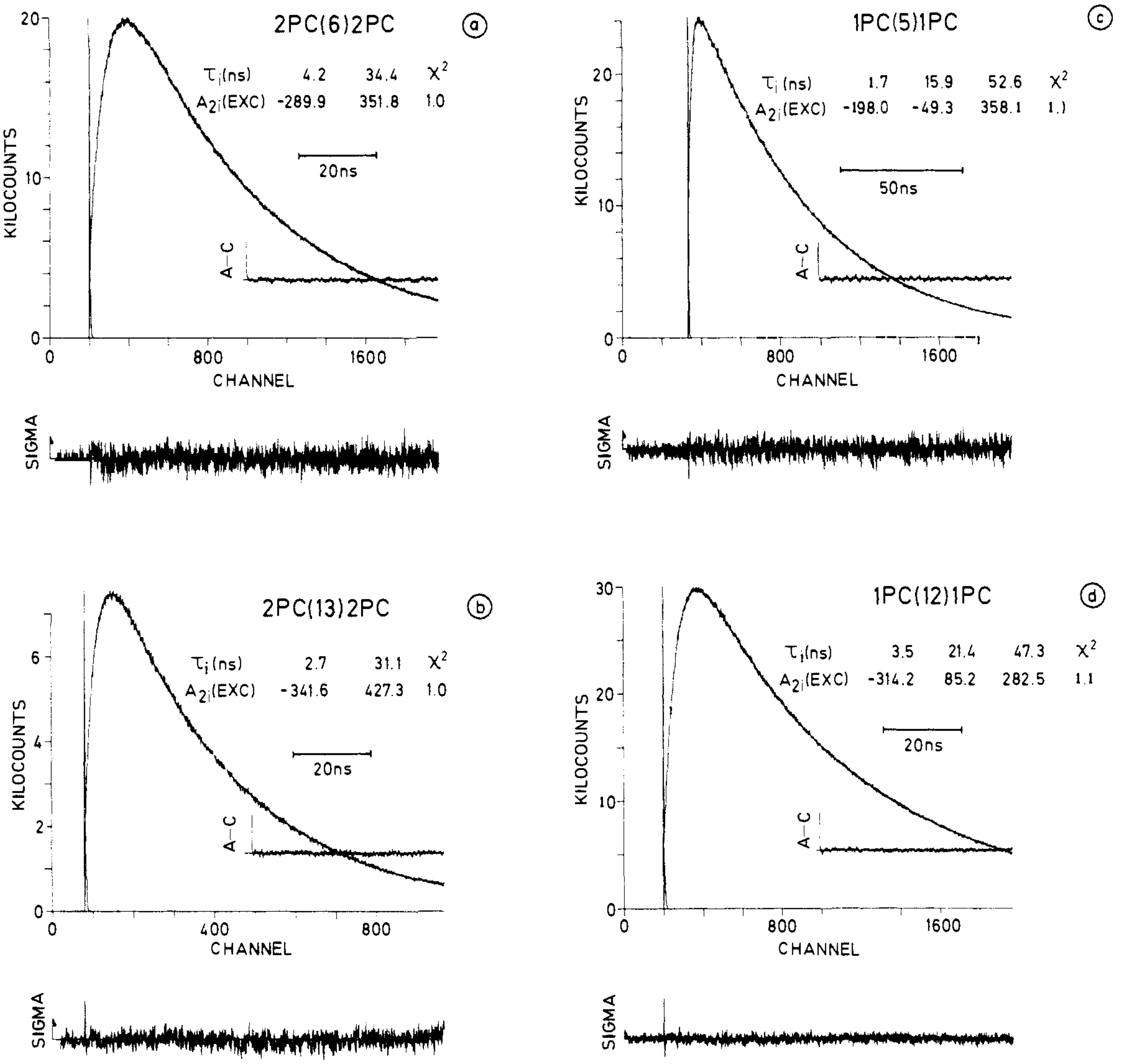

Figure 11. Excimer fluorescence response functions (at 520 nm) at 25 °C of (a) 1,6-bis(2-pyrenylcarboxy)hexane (2PC(6)2PC) in toluene, $R = 0.82$; (b) 1,13-bis(2-pyrenylcarboxy)tridecane (2PC(13)2PC) in toluene, $R = 0.80$; (c) 1,5-bis(1-pyrenylcarboxy)pentane (1PC(5)1PC) in n-octane, $R = 0.69$; and (d) 1,12-bis(1-pyrenylcarboxy)dodecane (1PC(12)1PC) in methylcyclohexane, $R = 0.86$. The values for the decay times τ_i and their preexponential factors A_{2i} are given, see eq 1. For the amplitude ratio $R = -A(-)/A(+)$, see text. The weighted deviations, σ (expected deviation), the autocorrelation function A–C and the value for χ^2 are also indicated.

through the chain. Secondly, a ring current effect leading to more positive δ values, similar to the downfield shifts of the protons in aromatic hydrocarbons.[14] These two contributions cannot be separated here. However, it has been observed[42] that in the related series of the diacetoxyalkanes, $H_3CCOO(CH_2)_nOOCCH_3$, the $\delta(\alpha\text{-}CH_2)$ of the compounds with the shorter chains ($n = 1$–7) likewise has a larger ppm value than that of the molecules with longer chains ($n = 8$–10 and 12). Similarly, in the series of acetic acid alkyl esters, $CH_3COO(CH_2)_nCH_3$, the chemical shift of the methyl group in the alkyl chain is a function of chain length, being shifted to larger ppm values for the shorter chains. For the octyl ester it just reaches the value observed for the CH_3 group in n-dodecane.[42,43] As ring current effects do not have to be considered in the two series of acetoxy compounds, it is concluded that the through-bond effect of the CH_3COO group extends over at least seven methylene units. This conclusion is supported by chemical shift data of the 1-alkylpyrenes $1Py(CH_2)_nCH_3$, where the influence of the pyrenyl group on $\delta(CH_3)$ is present up to 1-octylpyrene (Table III). These results indicate that in the PC(n)PC molecules the pyrenylcarboxyl groups likewise exert a through-bond interaction over up to eight CH_2 groups in the polymethylene chains.

Finally, the chemical shifts of the α-CH_2 groups in both series of bis(pyrenylcarboxy)alkanes have nearly identical values for every chain length, whereas with the dipyrenylalkanes 1Py(n)1Py and 2Py(n)2Py a substantial difference is observed in $\delta(\alpha\text{-}CH_2)$[12] for each n (Figure 12). This last difference is caused by the fact, already mentioned above, that in the frontier orbitals of pyrene a nodal plane passes through the carbon atom C2.[33-35] As a consequence, a 1-pyrenyl group exerts a stronger perturbation on the methylene groups than does a 2-pyrenyl moiety. This effect is apparently neutralized by the carboxy group in the PC(n)PC compounds.

Conclusion

From the chemical shift data for the aromatic protons in the two series of bis(pyrenylcarboxy)alkanes 1PC(n)1PC and 2PC(n)2PC with $n = 1$–16, 22, and 32 in chloroform-d at 24 °C, it is concluded that intramolecular ground-state dimers are present for $n = 3$–16 and $n = 3$–16, 22, and 32, respectively. This conclusion is based on the observation of shieldings, with respect to an appropriate model substance, for all pyrenyl protons. These shieldings are caused by ring current effects in conformers in which the pyrenylcarboxy groups adopt a dimer configuration. For the 2PC(n)2PC compounds with $n > 8$, the dimer has a symmetric sandwich structure, whereas with $n = 3$–8 the pyrenylcarboxy

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[42] Kühnle, W.; Reynders, P.; Zachariasse, K. A. Unpublished results.

[43] For the methyl group of the alkyl chain in the acetic acid alkyl esters $CH_3(CH_2)_nCOOCH_3$ in chloroform-d at 24 °C the following chemical shifts are found, as an example (ref 42): 0.893 ppm ($n = 5$) and 0.884 ppm ($n = 7$), whereas for n-dodecane 0.881 ppm (Table III) was measured.

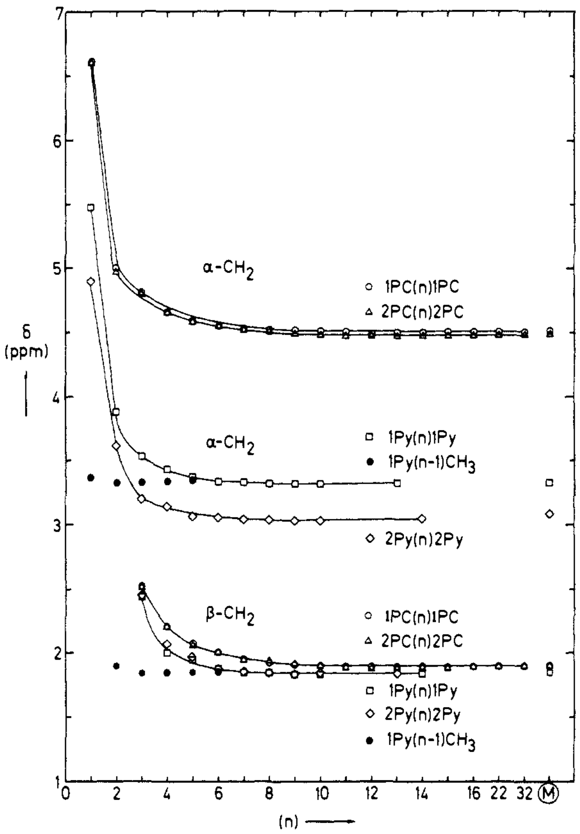

Figure 12. Chemical shifts δ (in ppm) for the methylene protons α-CH_2 and β-CH_2 in the alkane chains of the series of 1,*n*-bis(1-pyrenylcarboxy)alkanes (1PC(*n*)1PC) and 1,*n*-bis(2-pyrenylcarboxy)alkanes (2PC(*n*)2PC) with *n* = 1–16, 22, and 32 and of 1,*n*-di(1-pyrenyl)alkanes (1Py(*n*)1Py, *n* = 1–10, 13) and 1,*n*-di(2-pyrenyl)alkanes (2Py(*n*)2Py, *n* = 1–10, 14) in chloroform-*d* at 24 °C, as a function of the number of methylene groups (*n*) in the chain. The data for the model compounds M, 1PC(6) and 2PC(6), the hexyl esters of 1- and 2-pyrenecarboxylic acid as well as 1-octylpyrene and 2-ethylpyrene are also given. In addition, the δ values for a number of 1-alkylpyrenes are presented. See Tables I–III and ref 12.

moieties in the dimer are shifted along their long axis. In the case of the 1PC(*n*)1PC molecules, an asymmetric dimer is predominantly formed next to a symmetric one, especially for *n* = 3–7. From a comparison of the chemical shift differences Δδ(H4) of the bis(pyrenylcarboxy)alkanes with those of [4.4](2,7)pyrenophane, it is estimated that with 2PC(10)2PC in chloroform-*d* at 24 °C, as an example, around 6% of the molecules are present as ground-state dimers. For the PC(*n*)PC compounds with shorter chains (*n* = 3–8), larger −Δδ values are found, which points to a more pronounced dimer formation. With 1PC(5)1PC in octane-d_{18} the shielding of the pyrenyl protons and hence the dimerization is more important than in chloroform-*d* and also in toluene-d_8, which is explained by a better solvation of the end groups in the latter solvents. The Δδ pattern, i.e., the dimer structure, however, remains the same in the three solvents. Variation of the temperature, as studied with 2PC(5)2PC, likewise does not lead to appreciable changes in the shieldings.

The conclusions based on an analysis of ^1H NMR spectra are fully supported by results from time-resolved fluorescence measurements. In these SPC experiments, the ratio $R = -A(-)/A(+)$ of the negative to positive amplitudes in the excimer decays is smaller than unity with those PC(*n*)PC molecules for which dimer formation was inferred from the chemical shift data. In the case of 2PC(3)2PC, the presence of a ground-state dimer is seen from the dependence of its fluorescence spectrum on the excitation wavelength.

Mutual through-bond interactions of the pyrenylcarboxy groups in the PC(*n*)PC molecules do not affect the chemical shifts of the aromatic protons for *n* > 1, whereas the vicinal coupling constant $^3J_{23}$ is only influenced for *n* = 1–3. In the methylene chains of both series of the bis(pyrenylcarboxy)alkanes, PC(*n*)PC, the chemical shifts of the α- and β-CH_2 groups up to *n* = 8 and 9, respectively, have larger ppm values than those of the longer chains. This is attributed to a through-bond interaction coming from the second pyrenylcarboxy group, extending over eight CH_2 groups. Similar results are obtained for the dipyrenylalkanes.

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Registry No. 2Pc(1)2Pc, 126216-76-0; 2Pc(2)2Pc, 126216-77-1; 2Pc(3)2Pc, 126216-78-2; 2Pc(4)2Pc, 126216-79-3; 2Pc(5)2Pc, 126216-80-6; 2Pc(6)2Pc, 126216-81-7; 2Pc(7)2Pc, 126216-82-8; 2Pc(8)2Pc, 126216-83-9; 2Pc(9)2Pc, 126216-84-0; 2Pc(10)2Pc, 126216-85-1; 2Pc(11)2Pc, 126216-86-2; 2Pc(12)2Pc, 126216-87-3; 2Pc(13)2Pc, 126216-88-4; 2Pc(14)2Pc, 126216-89-5; 2Pc(15)2Pc, 126216-90-8; 2Pc(16)2Pc, 126216-91-9; 2Pc(22)2Pc, 126216-92-0; 2Pc(32)2Pc, 126216-93-1; 2Pc(6), 126216-94-2; 1Pc(1)1Pc, 126216-95-3; 1Pc(2)1Pc, 96157-36-7; 1Pc(3)1Pc, 96157-37-8; 1Pc(4)1Pc, 96157-38-9; 1Pc(5)1Pc, 96157-39-0; 1Pc(6)1Pc, 96157-40-3; 1Pc(7)1Pc, 96182-36-4; 1Pc(8)1Pc, 96182-37-5; 1Pc(9)1Pc, 96182-38-6; 1Pc(10)1Pc, 96182-39-7; 1Pc(11)1Pc, 96182-40-0; 1Pc(12)1Pc, 96182-41-1; 1Pc(13)1Pc, 96182-42-2; 1Pc(14)1Pc, 96157-41-4; 1Pc(15)1Pc, 96157-42-5; 1Pc(16)1Pc, 96157-43-6; 1Pc(22)1Pc, 96157-44-7; 1Pc(23)1Pc, 96182-43-3; 1Pc(6), 126216-96-4; 1MePy, 2381-21-7; 1EtPy, 17088-22-1; 1PrPy, 42211-33-6; 1BuPy, 35980-18-8; 1HxPy, 72692-89-8; 1OcPy, 71608-00-9; 1HxdPy, 80655-42-1; 1PhPy, 5101-27-9; 2Py(6)2Py, 126216-97-5; 2Py(7)2Py, 126216-98-6; 2Py(8)2Py, 126216-99-7; 2Py(9)2Py, 126217-00-3; 2Py(10)2Py, 126217-01-4; 2Py(12)2Py, 126217-02-5; 2Py(14)2Py, 126217-03-6; 2Py(1)2Py, 126217-04-7; 1Py(1)1Py, 96975-35-8; 1Py(2)1Py, 61577-80-8; 1Py(3)1Py, 61549-24-4; 1Py(4)1Py, 61549-25-5; 1Py(5)1Py, 61549-26-6; 1Py(6)1Py, 61549-27-7; 1Py(7)1Py, 126217-05-8; 1Py(8)1Py, 61549-29-9; 1Py(9)1Py, 61549-30-2; 1Py(10)1Py, 61549-31-3; 1Py(13)1Py, 61549-34-6; 2Py(2)2Py, 126217-06-9; 2Py(3)2Py, 97325-55-8; 2Py(4)2Py, 126217-07-0; 2Py(5)2Py, 126217-08-1; $CH_3CO_2CH_2O_2CCH_3$, 628-51-3; $CH_3CO_2(CH_2)_2O_2CCH_3$, 111-55-7; $CH_3CO_2(CH_2)_5CH_3$, 142-92-7; 2-ethylpyrene, 23801-18-5; 2-phenylpyrene, 5101-28-0; pyrene, 129-00-0; n-dodecane, 112-40-3; 2,7-dimethylpyrene, 15679-24-0; [2.2](2,7)pyrenophane, 57703-33-0; [3.3](2,7)pyrenophane, 88811-86-3; [4.4](2.7)pyrenophane, 88811-87-4.